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OF IONS BY ELECTROPHORETIC FOCUSING IONS**

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APPLICATION OF THE RETAINING ION TECHNIQUE TO SEPARATION
OF IONS BY ELECTROPHORETIC FOCUSING IONS

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Separation of lutetium and ytterbium by electrophoretic focussing ions can be achieved if copper ions are used in the cathodic solution containing the ligand, and also copper ions are added to the solution of rare earth ions which is to be spotted in the filter paper strip. The procedure is similar to the well known retaining ion technique developed by Spedding et al.³ in the case of ion exchange separation of rare earths elements.

INTRODUCTION

Electrophoretic focussing ions /E.F.I./ is an efficient separation technique based on paper electrophoresis of cations in a gradient of a complexing agent. The principles of E.F.I. separations have been described in detail by Schumacher.^{1,2} Such separations are achieved by using a ligand in the cathode compartment solution and a complex destroyer in the anode compartment solution. The anodic and cathodic solutions diffuse towards the center of a paper strip where the solution containing the ions to be separated has been placed. An electric voltage of several hundred volts is applied and after a few minutes sharp zones /focus/, containing the separated ions, are obtained. The relative locations of these focuses depend, mainly, on the stability constants of the complexes. For such

a reason, separation of ions whose values of the stability constants with the ligand used are very close, is not practical, if not impossible.

Friedli and Schumacher² calls attention to this fact in the case of the separation of lutetium and ytterbium by E.F.I., using ammonium salts of ethylenediaminetetraacetic acid /EDTA/ or nitrilotriacetic acid /NTA/ as complexing agents. Such a separation cannot be successfully achieved since the stability constants of both ions with EDTA /or with NTA/ are very close. The separation is not improved if the ammonium salts of both acids, EDTA and NTA, are contemporaneously used in the same solution.

Spedding et al.³ have shown that separations of adjacent rare earth elements by using ion exchange and EDTA can be highly improved if copper is used as retaining ion. Since E.F.I. and ion exchange separation techniques do have analogies, the ligand in E.F.I. playing the role exercised by the active exchangeable group of the resin, it was thought that the same retaining ion technique could be applied to E.F.I. in cases where the stability constants of the ions to be separated are very close to each other, such as in the case of the adjacent rare earth elements lutetium and ytterbium.

EXPERIMENTAL

The following solutions were used:

cathodic solution: sodium salt of NTA, 0.1M;
sodium salt of EDTA, 0.01M;
copper chloride, 0.01M;
pH of the solution: 4.7.
anodic solution: hydrochloric acid, 0.1M.

labelled solution of lutetium $^{177}\text{Lu}^*$ and ytterbium ^{169}Yb , $^{175}\text{Yb}^*$ at a concentration of 100 $\mu\text{g/ml}$ of each element /chloride salts/.

The rare earth solution was spotted on a Whatman 3 MM filter paper strip measuring 20 cm by 1 cm. To avoid spreading of the solution during the passage of the electric current the region where the solution was applied was located at about 2 cm from the center of the strip, in the anodic region. This region was chosen by running previous experiments with mixtures of lutetium and lanthanum, and observing the region where lutetium would be focussed. The experimental conditions for the separation experiment of lutetium and lanthanum were kept the same as when of the separation of lutetium and ytterbium. In some experiments copper ions /chlorides/ were added directly to the rare earths solution to be spotted in the filter paper strip.

A difference of potential corresponding to 700 volts was applied for various times from 10 to 60 min after which the paper strip was removed, dried and the detection of the focuses was made by autoradiography and by counting the strip cut into pieces of 2 mm width. A 400-channel analyzer and a NaI/Tl/ well-type scintillator were used for γ -counting. Scanning of the strips is better made by γ -counting rather than by radioautography due to poor resolution of the radioautographs in cases of too close foci.

*The radioactive isotopes were obtained by irradiating lutetium and ytterbium chlorides in a thermal neutron flux of about $5 \times 10^{12} \text{ ncm}^{-2} \text{ sec}^{-1}$ for 8 hrs; a cooling time of about 12 hrs was observed before use.

RESULTS AND DISCUSSION

By using only the mixture of sodium salts of EDTA and NTA, without copper, no separation could be achieved for the two adjacent rare earths lutetium and ytterbium. With copper

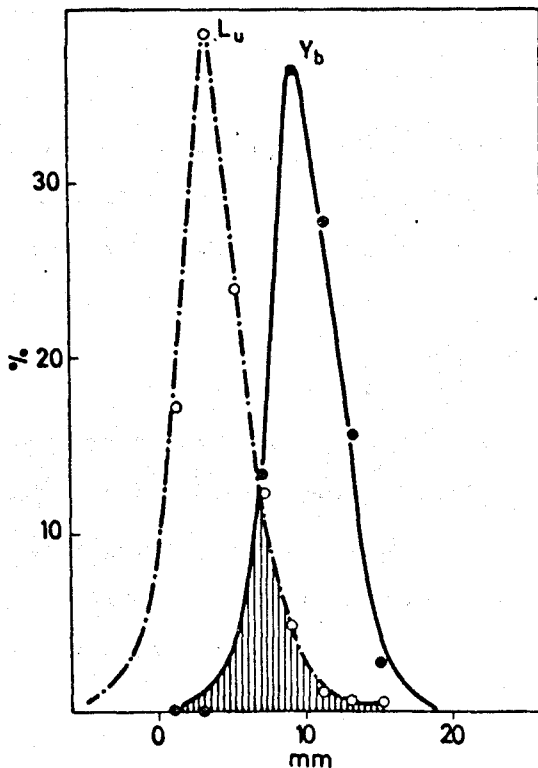


Fig.1. Percent of each element in the 2 mm fraction of electrophoresis paper

added to the cathodic solution, focussing of both elements was successful. Fig.1 is a typical separation obtained. The relative position of the focuses are in accordance with the stability constants of the EDTA and NTA complexes of lutetium and ytterbium.⁴ Purity of the isotopes in the various 2 mm pieces of the filter paper was checked by γ -spectrometry and half-life determinations.

Representation of the amount of the elements in the various 2 mm strips of paper is presented as percentage of the element, relative to its total, in that strip. An "enrichment factor", E, can be defined as the summation of the differences D of the percentage values $\%Lu - \%Yb$ or $\%Yb - \%Lu$, depending which value is the largest/ in each section or strip of the filter paper. Table 1 presents the values used for Fig.1 and for the calculation of the enrichment E in the lutetium and

TABLE 1

Percentage of total lutetium and ytterbium, and enrichment factor E for each element in the two focuses

Section	%Lu	%Yb	D	E /%
1	17.2	-	17.2	
2	38.9	-	38.9	
3	24.0	3.6	20.4	76.5
4	12.5	13.5	1.0	
5	5.0	36.5	31.5	
6	1.1	27.8	26.7	
7	0.6	15.8	15.2	
8	0.6	2.8	2.2	76.6
	99.9	100.0		

ytterbium foci. As seen in Table 1, an enrichment of about 76% for the region /about 6 mm/ where lutetium is concentrated, is obtained; the same value is found for the ytterbium region. Pure fractions for both elements were obtained, as seen from Fig.1. The crossed region, in Fig.1, is a region of cross-contamination.

If the concentration of copper solution used is too high /0.1M in Cu^{2+} / no separation is obtained, even with elements whose stability constants with EDTA are very different, such as lanthanum and lutetium. With such a concentration of the copper solution both elements do focus at the same point. By using a more dilute copper solution /0.05M in Cu^{2+} / some separation is obtained after 20 min. Best separations were obtained with copper solution of concentration corresponding to 0.01M in copper ions although the time for good focussing is about 60 min. This rather long time, as compared with the usual time for E.F.I., is no handicap for the process in the cases of separation of radioisotopes whose half-lives are not too short, such as in the case of lutetium and ytterbium.

Separations can be improved if, besides using copper ions in the cathodic solution, copper ions are also added to the original solution of the rare earth elements in such a way as to have copper ions concentration of the same order of magnitude as of the rare earth elements.

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RESUMO

Consegue-se a separação de lutécio e itérbio por meio da técnica de eletroforese focalizada usando íon cobre como cation de retenção. Os complexantes usados são os ácidos nitrilotriacéticos e etilenodiaminotetraacéticos, na forma de sais de sódio.

RÉSUMÉ

On a fait la séparation du lutetium de l'ytterbium, dans un mélange des deux éléments, par électroforese focalisée. Le cuivre est utilisé comme un ion de rétention par analogie avec la technique développée par Spedding et collaborateurs dans le cas de séparation des éléments de terres-rares par résine échangeuse d'ions.